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(19) (CA) **APPLICATION FOR CANADIAN PATENT** (12)

(54) Process for Producing Granulated Sodium Percarbonate

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(57) 7 Claims

Notice: This application is as filed and may therefore contain an incomplete specification.

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ABSTRACT OF THE DISCLOSURE

Sodium percarbonate of the formula 2 $Na_2CO_3 \cdot 3\ H_2O_2$ can be produced by fluidised-bed spray granulation by spraying an aqueous solution of sodium carbonate and a hydrogen peroxide solution on sodium percarbonate seeds and evaporating water. The previously necessary use of phosphorous-containing crystallisation inhibitor to prevent blockages and incrustations in and on the nozzle can be avoided by the invention if the solutions are sprayed using a single three-substance pulverisation nozzle with the external mixing of the solutions.

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Patent Claims

Process for the production of granulated sodium percarbonate of the formula 2 $Na_2CO_3 \cdot 3 H_2O_2$ by fluidised bed spray granulation, wherein an aqueous hydrogen peroxide solution and an aqueous sodium carbonate solution are sprayed by means of a three-fluid atomising nozzle comprising a nozzle body and a nozzle mouthpiece with external mixing of the solutions into a fluidised bed containing nuclei, the dimensions of which are smaller than those of the granulate particles to be produced, and water is simultaneously evaporated at a fluidised bed temperature in the range from 40 to 95°C,
characterised in that
a three-fluid atomising nozzle is used, the nozzle mouthpiece of which has a central tube and two jacket tubes arranged coaxially around the central tube and the central tube of which, at the nozzle tip, extends beyond the end of the jacket tubes by at least one radius of the central tube, and that one of the solutions is introduced into the central tube and one is introduced into the annular gap formed between the central tube and the inner jacket tube and a propellant gas is introduced into the outer annular gap formed between the jacket tubes.

2. Process according to claim 1,
characterised in that
a three-fluid atomising nozzle is used, the central tube of which nozzle mouthpiece extends beyond the end of the jacket tubes by 2 to 10, in particular by 3 to 6 radii of the central tube.

3. Process according to one of claims 1 or 2,
characterised in that
an aqueous hydrogen peroxide solution with an H_2O_2

content of 40 to 70 wt.% and an aqueous sodium percarbonate solution with an Na_2CO_3 content of 20 wt.% up to the saturation concentration are used.

4. Process according to one of claims 1 to 3, characterised in that the temperature of the fluidised bed is maintained in the range from 50 to 70°C.

5. Process according to one of claims 1 to 4, characterised in that spray granulation is performed in a continuously operated fluidised bed apparatus with an inlet for nuclei and a classifying granulate outlet.

6. Process according to one of claims 1 to 5, characterised in that granulated sodium percarbonate of the desired grain size is discharged from the fluidised bed apparatus at a moisture content of between 2 and 10 wt.% and, if required, is post-dried or passed for post-treatment in order to increase stability.

7. Process according to one of claims 1 to 6, characterised in that an aqueous soda solution and an aqueous hydrogen peroxide solution are introduced into the spray nozzle in a molar ratio of soda to H_2O_2 of 1:1.5 to 1:1.65.

Specification

This invention relates to a process for the production of granulated sodium percarbonate by fluidised bed spray granulation.

Various processing principles are known for the production of sodium percarbonate of the formula 2 $Na_2CO_3 \cdot 3 H_2O_2$: (i) reaction of hydrogen peroxide with sodium carbonate in the aqueous phase, crystallisation of the sodium percarbonate and separation thereof from the mother liquor; (ii) reaction of solid soda with aqueous hydrogen peroxide; (iii) fluidised bed spray granulation, wherein a hydrogen peroxide solution and a soda solution are sprayed in a fluidised bed apparatus onto sodium percarbonate nuclei and water is simultaneously evaporated. While the processing principle according to (i) is used on an industrial scale, auxiliary substances such as sodium chloride for salting out and metaphosphates to control crystallisation are, however, necessary and purification and/or partial discharge of the mother liquor is required in order to achieve good product quality. Due to irregularities and unsatisfactory storage stability, the quality of the sodium percarbonate produced using processing principle (ii) does not generally approach that of sodium percarbonate produced according to (i) or (iii).

Processes according to principle (iii) are attracting increasing interest as they give rise to no waste water and also result in an abrasion-resistant sodium percarbonate at very high yield. German patent 20 60 971 teaches such a

process: in this process, a sodium percarbonate solution or sodium percarbonate suspension or separately and simultaneously an aqueous hydrogen peroxide solution and an aqueous sodium carbonate solution are continuously introduced into a fluidised bed which contains sodium percarbonate nuclei, the dimensions of which are smaller than those of the granulate particles to be produced, and water is continuously evaporated from the aqueous medium containing sodium percarbonate and granulate particles of a certain size are removed from the fluidised bed. When a sodium percarbonate solution or an H_2O_2 solution and an Na_2CO_3 solution are used, nuclei are simultaneously fed into the fluidised bed.

The above-stated process exhibits a series of disadvantages: in one embodiment a sodium percarbonate solution or suspension must first be produced, which entails an additional process stage. Introducing a sodium percarbonate suspension or a supersaturated sodium percarbonate solution into a fluidised bed is liable to be troublesome because the spray nozzle used rapidly becomes plugged. On the other hand, if a dilute sodium percarbonate solution is used much water must be vaporised, so raising costs.

German patent 27 33 935 points out problems associated with another embodiment disclosed in DE 20 60 971 C3: when an aqueous hydrogen peroxide solution and an aqueous sodium carbonate solution are sprayed through two separate spray nozzles, such as conventional two-fluid nozzles for spraying a solution, using air as the propellant gas, it is difficult to achieve sufficiently intimate mixing of the two solutions in the fluidised bed, a feature which is however necessary in order to obtain homogeneous sodium percarbonate particles. However, if the two solutions are together introduced into the fluidised bed through a single spray nozzle, crystallisation occurs in the spray nozzle,

generally after a short period of operation, which gives rise to plugging and results in downtime.

In order to eliminate the above-stated problems, it is proposed in DE 27 33 935 C2 to use a common spray nozzle for both solutions and, in order to avoid plugging of the spray nozzle, to dissolve a metaphosphate in at least one of the two solutions. The two solutions are mixed within or at the inlet of the spray nozzle. The quantity of metaphosphate used is conveniently between 0.1 and 20 g per kg of sodium percarbonate.

On the one hand, the additional use of a metaphosphate in the process of DE 27 33 935 C2 increases raw material costs and, on the other hand, the phosphate introduced into the sodium percarbonate and thus into the detergents, bleaches and cleaning products containing the sodium percarbonate, is a component in which there is increasing interest in eliminating for environmental reasons.

The object of the present invention is thus to provide a process for the production of granulated sodium percarbonate of the formula 2 $Na_2CO_3 \cdot 3 H_2O_2$ by fluidised bed spray granulation, wherein an aqueous hydrogen peroxide solution and an aqueous sodium carbonate solution are sprayed using a single spray nozzle into a fluidised bed containing nuclei, the dimensions of which are smaller than those of the granulate particles to be produced, and water is simultaneously evaporated at a fluidised bed temperature in the range from 40 to 95°C, which process does not exhibit the disadvantages of the process known from DE 27 33 935 C2.

This object is achieved by using a three-fluid atomising nozzle with external mixing of the solutions for spraying the two solutions, to which no crystallisation inhibitor containing phosphorus is added.

A three-fluid atomising nozzle comprising a nozzle body and a nozzle mouthpiece is conveniently used, the nozzle mouthpiece of which has a central tube and two jacket tubes arranged coaxially around the central tube, wherein one of the solutions is introduced into the central tube and one into the annular gap formed between the central tube and the inner jacket tube and a propellant gas is introduced into the outer annular gap formed between the jacket tubes. According to a particularly preferred embodiment, a three-fluid atomising nozzle of the above-stated type is used having a central tube which, at the nozzle tip, extends beyond the end of the jacket tubes by at least one radius of the central tube.

By using a three-fluid atomising nozzle with external mixing, the two solutions each containing one reactant are sprayed into the fluidised bed by means of a single nozzle, wherein mixing of the two solutions and, thereafter, formation of the sodium percarbonate, occur outside the nozzle before the water evaporates from the liquid droplets. Sodium percarbonate particles of a homogeneous structure are obtained in this manner without the nozzle becoming plugged. By using a nozzle with a nozzle mouthpiece according to the invention and in particular such a nozzle with an extended central tube, it is possible to avoid encrustation on the nozzle tip and so possibly to avoid operational stoppages even after an extended period of operation. Simultaneously, it is possible to dispense with the use of a metaphosphate or another crystallisation inhibitor containing phosphorus, such that the granulated sodium percarbonate produced is substantially free of phosphorus compounds. A very low phosphorus content in the sodium percarbonate is not excluded in the event that hydrogen peroxide stabilised with phosphates, as is commercially conventional, is used.

The basic principle of the three-fluid atomising nozzle is similar to that known for conventional commercial two-fluid

nozzles, but it additionally contains devices for introducing and guiding the second liquid into the nozzle. The nozzle thus comprises a nozzle body with separate channels and connections for the media and a nozzle mouthpiece with the features according to the claims.

Figures 1 and 2 illustrate the structure of a convenient three-fluid atomising nozzle; the particularly preferred arrangement of the nozzle mouthpiece is simultaneously shown: figure 1 shows a longitudinal section of a particularly preferred three-fluid atomising nozzle; figure 2 shows a cross-section through the plane A-B shown in figure 1:

A nozzle body (1) is connected to a nozzle mouthpiece (2) in such a manner that the liquid media to be conveyed do not come into contact with each other until they are outside the nozzle. The connection between (1) and (2) may take the form of a plug, bayonet or screw fixing or sleeves or the like. In the preferred embodiment according to figure 1, the jacket tubes (11) and (12) of the nozzle mouthpiece are connected to the nozzle body by means of screw threads (9a and b). The nozzle body contains the connections (3) and (4) for the two liquids and (5) for the propellant gas, together with the separate channels (6) and (7) for the two liquids and (8) for the propellant gas.

The nozzle mouthpiece (1) comprises a central tube (10) and two jacket tubes (11) and (12) arranged coaxially around the central tube. The central tube (10) is connected with channel (7); in figure 1, channel (7) and the central tube (10) take the form of a continuous tube. The annular gap (13) formed between the central tube (10) and the inner jacket tube (11) is connected with channel (6) and the annular gap (14) formed between the inner (11) and outer (12) jacket tube is connected with channel (8). An essential feature of a particularly preferred embodiment is the central tube extension (15), which extends beyond the

ends of the jacket tubes at the nozzle tip. One or both jacket tubes and the central tube may taper inwards towards the nozzle tip ((17a) and (17b) in figure 1) in order to increase the exit velocity of the media and to promote break up of the liquid stream and propellant gas stream exiting from the annular gaps. The central tube (10) or its extension (15) and/or one or both of the annular gaps may additionally contain swirl inducers (16a and b). The propellant for the nozzle may be air or another inert gas, such as for example nitrogen or also superheated steam.

According to a preferred embodiment of the nozzle, the central tube of the nozzle mouthpiece extends beyond the ends of the jacket tubes by at least one radius of the central tube, preferably by 2 to 10, in particular 3 to 6 radii of the central tube. The jacket tubes preferably end at the same level. The jacket tubes may, however, also end at different levels, but the central tube extension according to the claims must be longer than both jacket tubes. Provided that the outer jacket tube extends beyond the inner jacket tube, the liquid in the annular gap and the propellant gas are premixed within the nozzle, but the liquids themselves do not come into contact with each other until they are outside the nozzle. The optimum size of the central tube extension is dependent upon the radius of the central tube and the flow area of the inner annular gap at the outlet. As the central tube radius increases, it is generally favourable to shorten the central tube extension; at a central tube radius of, for example, at least 2 mm, the central tube extension will generally be between 3 and 5 central tube radii.

In principle, the aqueous H_2O_2 solution or the Na_2CO_3 solution may be conveyed through the central tube of the nozzle and the other solution may be conveyed through the adjacent annular gap. Preferably, however, the solution present in the smaller volume (at preferred solution

concentrations, this will be the hydrogen peroxide solution) is passed through the central tube.

The aqueous hydrogen peroxide solution and the aqueous sodium carbonate solution are introduced into the fluidised bed maintained in an apparatus for fluidised bed spray granulation in a ratio such that the molar ratio of Na_2CO_3 to H_2O_2 is in the range between 1:1.4 and 1:1.7; a molar ratio of 1:1.5 and 1:1.65 is preferred.

The concentration of the solutions may vary over a broad range; the highest possible concentration is preferably selected in order to keep the quantity of water to be evaporated low. According to a particularly preferred embodiment, the Na_2CO_3 solution and the H_2O_2 solution will have a very high concentration, so that the sodium percarbonate solution initially present in droplet form in the mixing zone in front of the nozzle tip is supersaturated. The aqueous hydrogen peroxide solution conventionally contains from 30 to 75 wt.%, preferably 40 to 70 wt.%, of H_2O_2. The Na_2CO_3 concentration of the sodium carbonate solution is conveniently above 10 wt.% of Na_2CO_3, preferably between 20 wt.% and the saturation concentration at the particular temperature; Na_2CO_3 concentration is particularly preferably 30 wt.%. One or both solutions, but preferably the soda solution, may be used in preheated form at 30 to 70°C, instead of at a conventional storage temperature.

Reference is made to the cited prior art documents with regard to performance of fluidised bed spray granulation. In the case of continuous operation, a sufficient number of nuclei must always be present in the fluidised bed. In order to control grain size distribution, between 0 and 30 kg, preferably between 1 and 10 kg of nuclei are introduced into the fluidised bed per 100 kg of granulated sodium percarbonate discharged from the fluidised bed. The weight of nuclei is determined by the desired grain size

range and in particular by the size of the nuclei. It is necessary to optimise operating conditions with regard to the introduction of nuclei at a given desired fluidised bed temperature in order to achieve steady state operation. Recirculating an excessively large quantity of very finely divided material as nuclei may result in excessively low particle growth, while an excessively high moisture content in the fluidised bed may result in unwanted aggregation. Reference is made to the article by H. Uhlemann in *Chem.-Ing. Technik* 62 (1990), no. 10, pp. 822-834 with regard to the general technique of fluidised bed spray granulation, the mutual interaction of operating parameters and control of particle size and distribution and to suitable equipment for continuous fluidised bed spray granulation.

The temperature of the fluidised bed is maintained between 40 and 95°C, preferably between 40 and 80°C and in particular between 50 and 70°C.

The temperature of the inlet air for drying and maintaining the fluidised bed is adjusted to above 120°C, preferably between 200 and 400°C and in particular between 300 and 400°C. The person skilled in the art will adjust the temperature and mass flux of the inlet air in such a manner that a well fluidised bed is produced, the required performance may be achieved and an excessively large quantity of product need not be returned from a downstream dust separator. The velocity of the drying air in the empty tube is conventionally between 1 and 4 m/s. The fluidised bed apparatus is generally operated in such a manner that approximately standard pressure (around 1 bar) prevails in the area of the fluidised bed; it is, however, also possible to operate at a pressure below or above standard pressure. One or more three-fluid atomising nozzles may be arranged in the fluidised bed spray granulation unit, wherein the direction of spraying may be substantially cocurrent or countercurrent to the stream of drying air or may assume an intermediate position.

It has proved convenient in the case of continuous operation to discharge the sodium percarbonate at a residual moisture content of up to 10 wt.%, preferably of between 3 and 9 wt.% and in particular between 5 and 8 wt.% and, if desired, to dry it in a downstream apparatus to the residual moisture content of the conventional commercial product (below 1 wt.%) or to pass it on for post-treatment. Post-treatments which may in particular be considered are processes for providing a shell around the particles for the purpose of increasing storage stability. Such post-treatment is preferably based on applying solutions containing one or more shell components, such as for example boron compounds, soda, sodium sulphate, magnesium sulphate and water glass onto the previously produced granulated sodium percarbonate in a fluidised bed while simultaneously evaporating water and forming a firmly attached outer shell.

If required, the H_2O_2 solution and/or Na_2CO_3 solution to be sprayed may also contain additives (with the exception of crystallisation inhibitors containing phosphorus) in order to influence product properties and in particular to increase the active oxygen stability of the hydrogen peroxide used and of the sodium percarbonate to be produced. Stabilising additives which may be considered are preferably magnesium salts (conventionally added to the H_2O_2 solution in sulphate form) and water glass (usually added to the soda solution); further additives may be, for example, stannates, complexing agents and dipicolinic acid. While phosphorus-free crystallisation inhibitors may be present, they are not conventionally used. Speed of dissolution may, for example, be increased by adding surface-active substances.

The apparatus for fluidised bed spray granulation may be those as are described in DE 27 33 935, EP 0 332 929 B1 and in the already cited article by H. Uhlemann. The fluidised bed may be equipped with one or preferably with two or more

three-fluid atomising nozzles according to the invention. Apparatus having an inlet for nuclei and a classifying granulate outlet is preferred. The nuclei to be introduced into the fluidised bed may originate from dust separation, screening and/or partial comminution.

In addition to the above-stated apparatus having a steady state fluidised bed, the process may also be performed in a fluidised bed flow channel, which is equipped with one or more nozzles arranged in series; the product is classified at the end of the flow channel and undersized product, optionally together with comminuted oversized product, is returned to the flow channel.

Although the process of the invention is preferably performed continuously on an industrial scale, *i.e.* with continuous introduction of the solutions and discharge of the granulated product of the desired size, it may also be operated discontinuously (spraying terminated once the desired grain size range has been achieved and the granulated product is then discharged).

It is possible by means of the process according to the invention to obtain granulated sodium percarbonate starting from a hydrogen peroxide solution and a sodium carbonate solution by fluidised bed spray granulation on an industrial scale without stoppages due to plugging or encrustation of the nozzles in a virtually quantitative yield with an elevated active oxygen content, elevated abrasion resistance, elevated bulk density and very good storage stability without there being any need to use crystallisation inhibitors. In order to increase stability, the product obtainable according to the invention may, immediately after production, be enclosed in a shell in a manner known *per se*, wherein due to the dense and substantially spherical structure of the grains, a smaller quantity of shell material than is required for enclosing

sodium percarbonate obtained by crystallisation processes in a shell is sufficient.

It could not be predicted that it would be possible by using a three-fluid atomising nozzle according to the invention not only to achieve adequate external mixing of the solutions and to obtain a homogeneous product, but also to dispense with a crystallisation inhibitor containing phosphorus; operating costs are thus reduced and an environmental problem is avoided. It was moreover not to be expected that by using a three-fluid atomising nozzle with a central tube extension it would be possible virtually completely to avoid stoppages due to encrustation on the nozzle.

Examples

An aqueous hydrogen peroxide solution and an aqueous sodium percarbonate solution, which contained no crystallisation inhibitors, were introduced into a fluidised bed using air as the propellant in an apparatus for fluidised bed spray granulation with devices for dust recirculation and the introduction of nuclei and a classifying granulate outlet, once an initially introduced quantity of sodium percarbonate had been fluidised. The nozzles were located within the fluidised bed and the direction of spraying was cocurrent with the stream of drying gas. The central tube extension was 3 central tube radii in length, the jacket tubes ended at the same level.

The table shows the essential operating parameters and material data for the sodium percarbonate produced. Even after several days' continuous operation, there was no plugging or encrustation in or around the nozzle.

Example no.			Input			Output			Screen analysis			
	FB holdup[1] (Gt/h)	FB temp.[1] (°C)	Soda solution[2] (Gt/h)	H_2O_2 solution[3] (Gt/h)	Nuclei[4] (Gt/h)	NaPc[5] (Gt/h)	Oa[6]	Moisture (%)	>0.8 mm	0.6-0.8 mm	0.2-0.6 mm	< 0.2 mm
1	approx. 100	57	120	43	8	61	13.8	4.3	4.2	80.7	13.5	1.6
2	approx. 100	57	120	43	7	60	13.7	4.1	3.8	40.2	53.6	2.4
3	approx. 100	57	120	29	9	64	13.5	6.3	6.7	85.2	7.6	2.4
4	approx. 100	58	225	55	14	118	13.6	5.4	22.3	75.0	2.4	0.3
5	approx. 100	59	225	55	0	105	13.9	2.5	1.7	12.1	84.1	2.1
6	approx. 100	59	225	55	12	131	13.5	7.6	7.2	84.6	7.6	0.6
7	approx. 100	59	225	55	0	121	13.5	7.5	90.2	8.6	1.1	0.1
8	approx. 100	59	225	60	12	130	13.7	7.3	7.6	86.2	5.7	0.5

Gt/h = parts by weight/hour; NaPc = sodium percarbonate

1) Product quantity and temperature in fluidised bed

2) Concentration: 30 wt.% Na_2CO_3; temperature of solution 35°C

3) Examples 1 to 3: concentration = 40 wt.% H_2O_2; examples 4 to 8: concentration = 60 wt.% H_2O_2

4) Ground product with a grain size range between 0.05 and 0.2 mm were introduced as nuclei

5) A certain degree of solids loss was experienced due to a dust separator which was not adapted to the product.

6) Active oxygen content of the discharged moist sodium percarbonate

List of reference numbers

1	Nozzle body
2	Nozzle mouthpiece
3	Connection for liquid (i)
4	Connection for liquid (ii)
5	Connection for propellant gas
6	Channel for liquid (i)
7	Channel for liquid (ii)
8	Channel for propellant gas
9a	Thread
9b	Thread
10	Central tube
11	Jacket tube (inner)
12	Jacket tube (outer)
13	Annular gap for liquid (i)
14	Annular gap for propellant gas
15	Central tube extension
16a	Swirl inducer
16b	Swirl inducer
17a	Taper
17b	Taper

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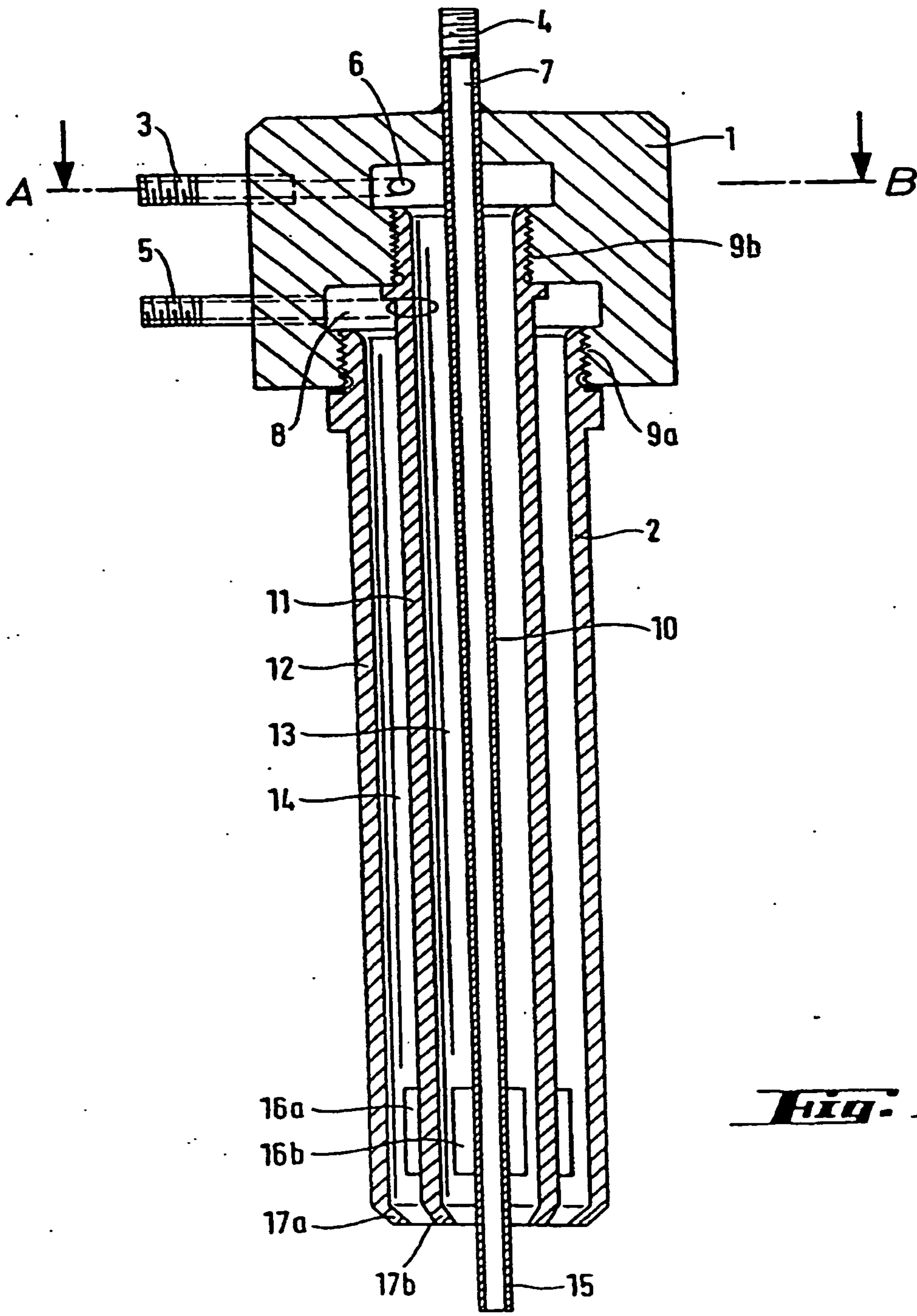

Fig. 1

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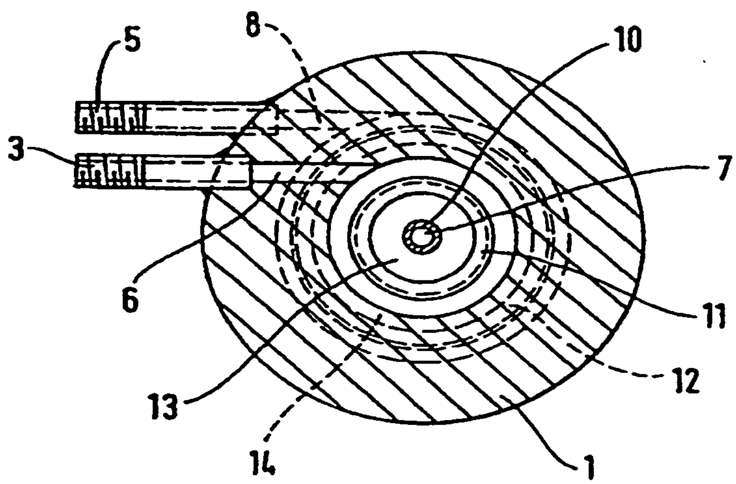
Fig. 2

(A-B)



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